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Theoretical study on mechanical and electron-transport properties of conjugated molecular junctions with carboxylic or methyl sulfide links

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ABSTRACT

The mechanical and electronic transport properties of 4-(methylthio)benzoic acid (M1), 1,4-bis(methylthio) benzene (M2) and methyl 4-(methylthio)benzoate (M3) molecular junctions are studied employing density functional theory and elastic scattering Green's function method. The numerical results show that the rupture force of M1 and M2 junctions are both about 0.6 ± 0.1 nN as experiment probed, which is much smaller than the force to break COO^-–Au bond. The COO^- group strongly influenced on M1 molecular junction and further strengthened SMe–Au bond at the other end of the junction. The M3 junction is less stable because the CH_3 group linked to COO group destroyed the mechanical stability of COO–Au connection. The conductance of M2 junction is about an order larger than that of M1 junction as the experiment probed. The less stable feature of M3 junction leads the absence of conductive peak.

1. Introduction

Due to the rapid progress of single-molecule-manipulation technology, such as mechanically controllable break junctions (MCBJ) [1–5], scanning tunneling microscopy (STM) [6–8], atomic force microscopy (AFM) [9–13] and the combined technology of them in the last decade [3], single organic molecular junctions have been designed and probed extensively, which provides intrinsic understandings in functional properties of molecular devices [4, 13–21]. As is well known, the evident quantum effect of micro system induces the uncertainty of interface structures between functional molecule and metal electrodes [22], which further brings difficulty to experiment to construct stable molecular junction and make the results of experimental measurement various from one to one [23]. In order to understand the formations of molecular junctions and design valuable molecular devices, researchers investigated different kinds of molecular junctions with different link groups to attach molecules to gold electrodes [11,24–28]. These investigations indicated that the rupture force of the molecular junction with thiol links is varied from 1.0 nN to 1.7 nN [29]; however, the rupture force is about 0.6–0.8 nN for the molecular junctions with amine, methylsulfide, and diphenylphosphine linkers which bind to gold through donor–acceptor bonds [30]. Carboxylic acid group (COOH) is also an attractive linker since it has various chemical modification possibilities [24,31,32]. However, because of the low solubility in most non-polar organic solvents, only a few electronic measurements of conjugated systems with COOH terminal groups are carried out [33,34]. Recently, Ahn S. and his co-workers overcame practical challenges to measure electronic and mechanical properties of conjugated molecules terminated with both COOH and SMe (methyl sulfide) links [34]. They found that, the electronic transport properties of Au–molecule–Au junction with SMe terminal group are comparable to the junction with COOH termination. They also concluded that COO^-–Au bond is comparable to Au–SMe bond from the measurement results that the rupture force of Au–molecule–Au junction with both SMe and COOH groups is comparable to the bond rupture force of di-SMe terminated molecular junction. Considered that these experimental results and corresponding conclusions are very interesting and significant, in this paper, we construct Au–molecule–Au junctions using three different conjugated molecules that Ahn S. et al. probed [34], and simulate the elongate and rupture process basing on the first-principles calculations. The electronic transport properties of those molecular junctions are also investigated by applying generalized elastic scattering Green's function method that we developed [35,36]. Our theoretical simulations provide insight into the mechanics and electronics properties of these molecular junctions, and especially elucidate the questionable problems that existed in the experiment deductions.

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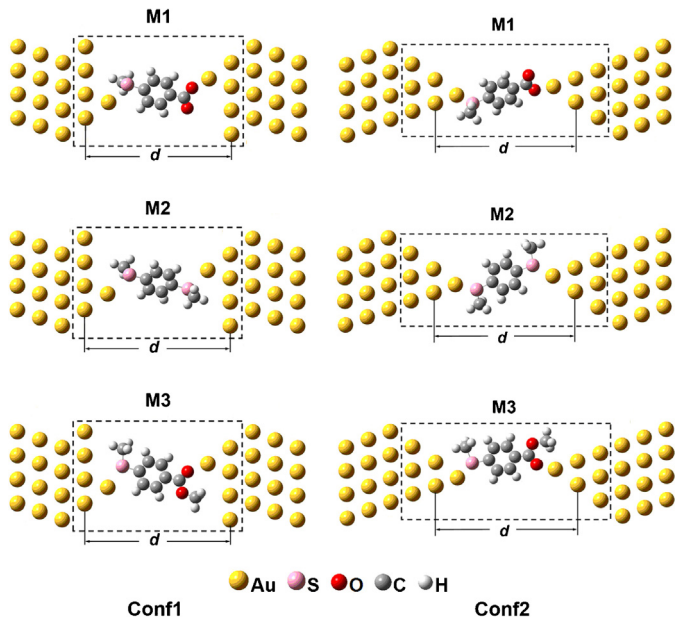

Fig. 1. Schematic structure of molecular junction with two configurations, Conf1: A single Au atom on Au(111) surface, the S atom of terminal SMe group or terminal O atom is adjacent to this single Au atom, while the terminal methyl is beside it; Conf2: Ideal gold tips are formed, the terminal S or O atom is also adjacent to the single tip Au atom, however the terminal methyl is beside the gold tips. The dashed box denotes the extended molecules that perform first-principles computation to obtain coupling between molecule an electrode.

2. Theoretical model and computational detail

The molecules that we study are 4-(methylthio)benzoic acid (M1), 1,4-bis(methylthio)benzene (M2) and Methyl 4-(methylthio) benzoate (M3). As we know, the semi-infinite electrode is impossible to be completely considered in the first-principles simulation. Hence in order to simulate the effect of electrode on molecule, considering the screening effect of inner gold layers and the reliability of the results, in the computation, we select suitable number of gold atoms which are close to the functional molecule to form gold atom cluster, and then sandwich the molecule between two gold atom clusters to form Au–molecule–Au extended molecule (denoted by dashed box in Fig. 1) to simulate molecular junction. Due to the interaction between molecule and electrodes, one can expect when fabricate gold electrodes in the experiment, different tip configurations may be formed [23], such as wide flat surface tip, wide surface tip with a few defect Au atoms on it or very sharp gold tip. Based on our calculation, the molecule with SMe links is difficult to anchor on flat gold surface due to the influence of methyl in the end SMe group. However, when construct molecular junction, the molecule is more likely absorbed on the sharp tip site or on the edge site of surface defect Au atom. So in this study we design two representative interface configurations for each molecular system (Fig. 1). For the first configuration (denoted as Conf1, left three molecular junctions in Fig. 1), there is a single Au atom on the Au(111) surface of gold electrode which simulate surface defect Au atom, the S atom of terminal SMe group or O atom of terminal COO^- group is adjacent to single surface Au atom, while the terminal methyl is beside this single surface Au atom on the second layer of Au atoms. For the second configuration (denoted as Conf2, right three molecular junctions in Fig. 1), the gold electrodes form ideal sharp tip configurations, the S atom of terminal SMe group or O atom of terminal COO^- group is adjacent to single tip Au atom, while the terminal methyl is beside the gold tip. It should mention that the COOH group link to gold through COO^-–Au bond. Then we fix the distance of gold electrodes and perform geometric optimization of the molecular

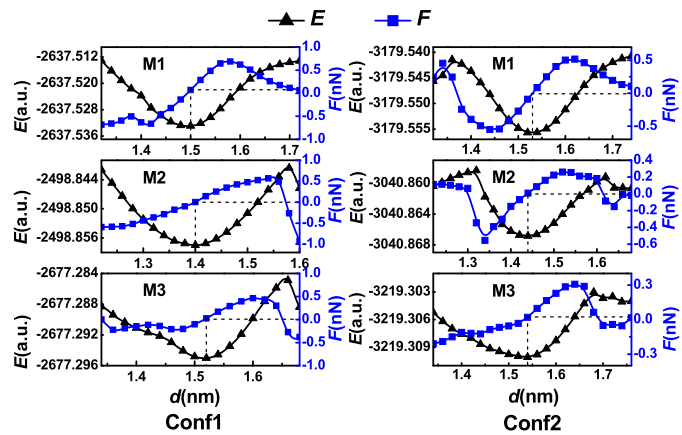

Fig. 2. Ground-state energy (E) and force (F) as functions of the distance (d) between two electrodes.

systems. Using the single point energy (denoted as E) and the corresponding electrodes distance, we obtain the force between the electrode and the functional molecule by the formula $F = \partial E/\partial d$, where d is the electrode distance as is shown in Fig. 1.

Based on the general Green's function formalism of Mujica et al. [37], the net current density of molecular junctions from source to drain can be written as [35,36,38]

$$i_{SD} = \frac{4em^* k_B T}{\hbar^3} \int_{eV_{SD}}^{\infty} \ln \frac{1 + \exp[(E_f + eV_{SD} - E_z)/k_B T]}{1 + \exp[(E_f - E_z)/k_B T]} \times \left|\tau(E_z, V_{SD})\right|^2 n^S(E_z) n^D(E_z)\, dE_z \quad (1)$$

where V_{SD} is external bias, m^* is effective mass of electron, E_f is the Fermi level, n^S and n^D are the density of states of source and drain. The transition matrix element from the source to the drain is

$$\tau(E_z, V_{SD}) = \sum_J \sum_K U_{JS}(V_{SD}) U_{KD}(V_{SD}) \times \sum_n \frac{\langle J|n\rangle\langle n|K\rangle}{[E_z - E_n(V_{SD})] + i\Gamma_n} \quad (2)$$

where $|n\rangle$ is an eigenstate of the Hamiltonian (H) of a finite system that consists of the molecule sandwiched between two clusters of metal atoms. The summation of n runs over the eigenstates whose energies are higher than the Fermi level. J and K run over all atomic sites. Γ_n is the energy broadening. U_{JS} (or U_{KD}) is the coupling energy between an atomic site J (or K) and an electron reservoir S (or D). The current is obtained as $I_{SD} = Ai_{SD}$, where A is the effective injection area [39,40] and the conductance is $G = \partial I_{SD}/\partial V_{SD}$.

The geometric optimizations and the electronic structure are computed at the B3LYP level with Lanl2DZ basis set in Gaussian03 packages [41]. The QCME codes [42], which based on the generalized quantum chemical Green's function theory [35,36], are used to carry out the electron-transport properties.

3. Results and discussion

3.1. Stretching processes and mechanical properties of the molecular junctions

The elongating process and the formation of molecular junctions are simulated by adjusting the distance between the two electrodes. Plots of the Ground-state energies (E) and forces (F) as functions of electrode distance (d) are shown in Fig. 2. The energy curves show that the minimal energies occur at $d = 1.50$, 1.40,